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Addition reactions of fluoroalkanesulfonyl azides to [60] fullerene under thermal or microwave irradiation condition

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ABSTRACT

The reactions of [60] fullerene with excess fluoroalkanesulfonyl azides $R_fSO_2N_3$ in *o*-dichlorobenzene under thermal or microwave irradiation condition afforded monoadduct opened [5,6]-bridged azafulleroids. While, similarly treatment of 2,2,2-trifluoroethyl azides $CF_3CH_2N_3$ with C_{60} gave two monoadducts, i.e., opened [5,6]-bridged azafulleroids, closed [6,6]-bridged Aziridino-fullerene, and some multi-addition product. A general mechanism for these addition reactions was proposed.

1. Introduction

The reactions of organic azides with [60] fullerene have paved the way for the synthesis of adducts with a variety of structure.[1–6] The first example of reaction was reported by Wudl et al.[1] Till now, it is well established that this reaction involved a [2+3] cycloaddition of azide to a double bond of the fullerene with formation of intermediate triazoline, followed by thermal cleavage of N_2 affording the opened [5,6]-bridged azafulleroid or closed [6,6]-bridged aziridino-fullerene depending on the nature of the substituent of the azide. Alternatively, nitrenes generated in situ by thermolysis or photolysis of azides add to fullerene in [1+2] cycloaddition yielding closed [6,6]-aziridino-fullerene derivatives.[7–9] Recently, Mattay and Ulmer[10] reported the preparation of sulfonylazafulleroid and aziridino-fullerene derivatives by thermal reactions of excess sulfonyl azides RSO_2N_3 (R: CH_3, $C_6H_5CH_2$, *p*-$CH_3C_6H_4$, *p*-$MeOC_6H_5$) with C_{60}.

To the best of our knowledge no addition reaction of fluoroalkanesulfonyl azides $R_fSO_2N_3$ **1** with C_{60} are known. During our study on the fluoronated sulfonyl azides **1**, we found that they are readily reacted with many aromatic compounds and electron rich olefins such as silylenol ether, acyclic or cyclic vinylether, enamines, etc.[11–15]

Fullerene C_{60} was considered as electron-deficient compound,[16] its reaction with **1** should be under more violent condition. As part of our continuing interest in the chemical transformation of fluoroalkanesulfonyl azides, we now report our preliminary investigation of the first reaction of C_{60} with fluorinated azides and discuss the possible reaction mechanism.

2. Results and discussion

Thermal reaction of C_{60} (0.11 g, 0.14 mmol) with an equal molar azide $ICF_2CF_2OCF_2CF_2SO_2N_3$ **1a** was first carried out in

Table 1
Reaction of **1a** with C_{60} under different conditions

Entry	Reaction conditions				Yield[d] of **2a** (%)
	Mol. ratio[a]	Solvent	Temp (°C)	Time (h)	
1	1	CB[b]	130	2	—[e]
2	4	CB	130	2.5	5[e]
3	11	CB	130	2.5	16[e]
4	4	*o*-DCB[c]	160	1.5	15
5	11	*o*-DCB	160	2	26
6	12	*o*-DCB	160	2	30

[a] Ratio of **1a**/C_{60}.
[b] CB: chlorobenzene.
[c] *o*-DCB: *o*-dichlorobenzene.
[d] Isolated yield based on the reacted C_{60}, all reactions gave $R_fSO_2NH_2$ **3**.
[e] Small amount of **4**.

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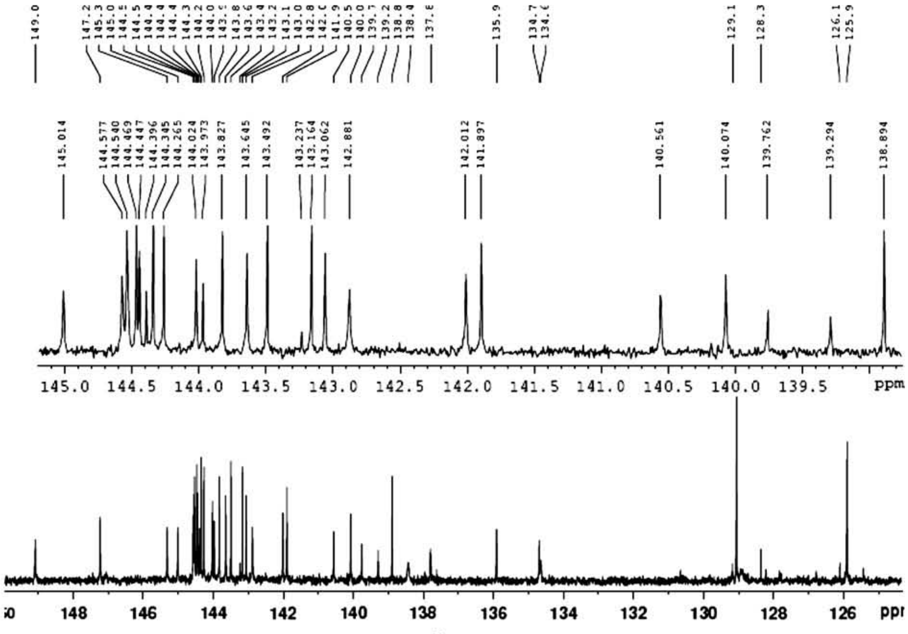
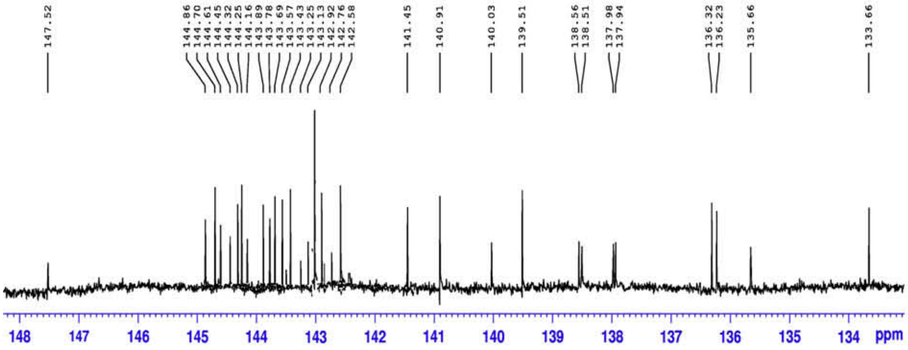
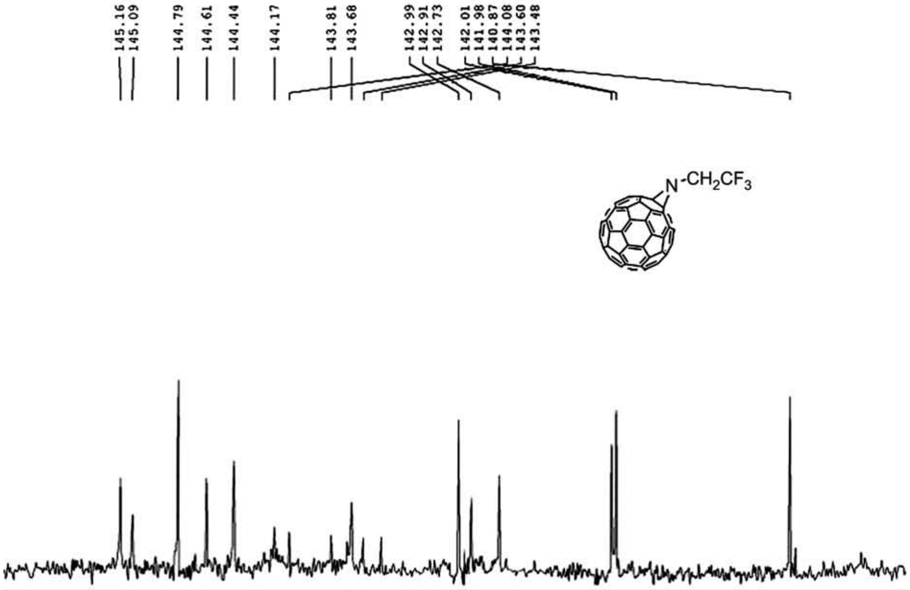


2a ^{13}C NMR



5a ^{13}C NMR



5b ^{13}C NMR

Figure 1. ^{13}C NMR of **2a**, **5a**, and **5b**.

chlorobenzene (30 mL) after stirring the reaction mixture for 2 h at 130 °C, the reaction was finished, chromatography on silica gel gave unconverted C_{60} first, more polar products obtained by using AcOEt/petroleum ether as elute were the corresponding fluoroalkane-sulfonylamine $ICF_2CF_2OCF_2CF_2SO_2NH_2$ **3a** and small amount of $ICF_2CF_2OCF_2CF_2SO_2NH–C_6H_4Cl$ **4**, which was identified with author's sample,[15] no corresponding C_{60} addition product was isolated and detected.

When the molar ratio of **1a** to C_{60} was increased from 1:1 to 4:1 and then to 11:1, the addition product **2a** was obtained and the yield was 5% and 16%, respectively (see Table 1, entries 1–3). The main product remained was the sulfonylamine **3a**. In order to increase the reaction temperature, *o*-dichlorobenzene (*o*-DCB) was used as solvent. Under higher temperature (160 °C) and excess azide (up to 12 equal molar ratio), the yield of **2a** was increased up to 30% (Table 1 entry 6), it was noticed that there is no corresponding *N*-fluoroalkanesulfonyl dichloroaniline $R_fSO_2NHC_6H_3Cl_2$ formed.

The structure of **2a** was identified by spectroscopic methods. The ^{13}C NMR of **2a** shows 32 signals at 125.90–149.08 ppm (Fig. 1, ^{13}C NMR of **2a**). In this spectrum, 28 signals have a relative intensity of 2 and the remaining 4 signals have the intensity of 1, the total integrated area for the aromatic region sums up to 60 carbon atoms.[1] Because all the fullerene carbons are in the sp^2 region the product **2a** is the opened [5,6]-bridged azafulleroid with the C_s-symmetry rather than the closed aziridine structure. The remaining very weak signals are all t–t patterns and attributed to the fluorocarbon atoms CF_2. Further evidence is obtained from the UV–vis spectrum, which is similar to pure C_{60}, the characteristic absorption for [6,6]-closed fullerene derivatives at 420 nm is not observed.[17–19]

The ^{19}F NMR spectrum of **2a** is very similar to the starting azide **1a** with a small downfield shift due to the electron-deficient influence of the carbon sphere.[1] TOF mass of the monoadduct **2a** shows a weak molecular ion peak M^- at $m/z=1140.8$.

Under the optimum reaction conditions (Table 1, entry 6) other fluoroalkanesulfonyl azides **1b** and **1c** added to C_{60} giving the monoadducts [5,6]-opened ring azafulleroid **2b** and **2c** in 25% and 18% yield, respectively (see Table 2).

When the reaction of **1** with C_{60} in *o*-DCB was conducted under microwave irradiation (700 W), the same product azafulleroids **2** and fluoroalkanesulfonyl amine **3** were isolated. The yields of **2a**, **2b**, and **2c** were 32%, 16%, and 21%, nearly the same as the thermal reactions, but the reaction time was shortened from 2 h to 20 min.

In contrast to the fluoroalkanesulfonyl azides **1**(**a**–**c**), fourfold excess of 2,2,2-trifluoroethyl azide $CF_3CH_2N_3$ **1d** added to C_{60} affording not only two monoadducts, *N*-trifluoroethyl azafulleroid **5a** and aziridino-fullerene **5b**, but the multi-addition products **5c** and **5c′** as well, it was also noted that in this reaction no corresponding $CF_3CH_2NH_2$ was formed. The ^{13}C NMR spectrum of **5a** and **5b** shows the big difference (Fig. 1, ^{13}C NMR of **5a** and **5b**). The spectrum of **5a** is similar to the azafulleroid **2a** exhibiting 32 signals at 133.66–147.52 ppm for the sp^2 carbons of the C_{60} skeleton, and two sp^3 carbon atoms at 125.06 and 54.10 ppm for CF_3 and CH_2. While the spectrum of **5b** exhibits only 16 peaks at 140.9–145.2 ppm for the sp^2 carbons and one peak at 82.3 ppm for the sp^3 hybridized carbons of C_{60} skeleton, other two peaks at 125.06 and 51.35 ppm are attributed to the two sp^3 carbon atoms CF_3 and CH_2. This indicates for compound **5b** C_{2v}-symmetry with a [6,6] junction on the fullerene core. The UV–vis spectrum of **5b** exhibits the typical absorption for [6,6]-bridged dihydrofullerenes including the band at around 422 nm (Fig. 2).[9,10]

Table 2
Reaction results of azides **2** with C_{60} under thermal or microwave irradiation

Entry	Reactant	Ratio[a]	Method[b]	Time	Products	Yield[c] (%)
1	**1a**	12	A	2 h	**2a**	30
2	**1a**	11	B	20 min	**2a**	32
3	**1b**	12	A	2 h	**2b**	25
4	**1b**	11	B	20 min	**2b**	16
5	**1c**	12	A	2 h	**2c**	18
6	**1c**	11	B	20 min	**2c**	21
7	**1d**	4	A	3 h	**5a**	48
					5b	16
					5c	5
					5c′	12
8	**1d**	4	B	20 min	**5a**	38
					5b	19

[a] The molar ratio of azides to C_{60}.

[b] Method A: heating in *o*-DCB at 160 °C for **1**(**a**–**c**) or 120 °C for **1d**; method B: irradiated under microwave (700 W).

[c] Isolated yield based on the reacted C_{60}.

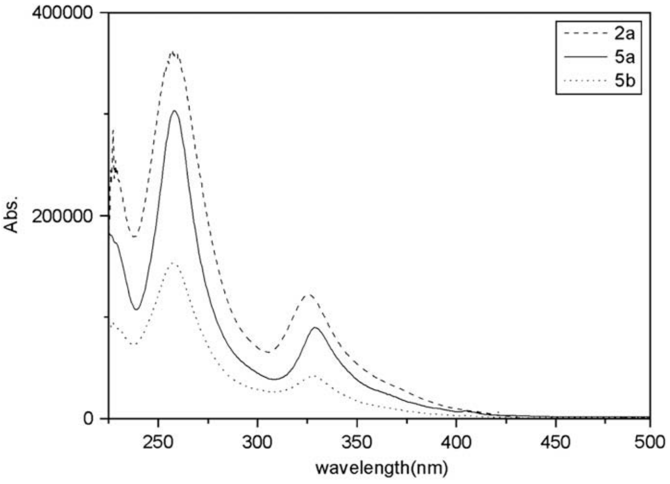
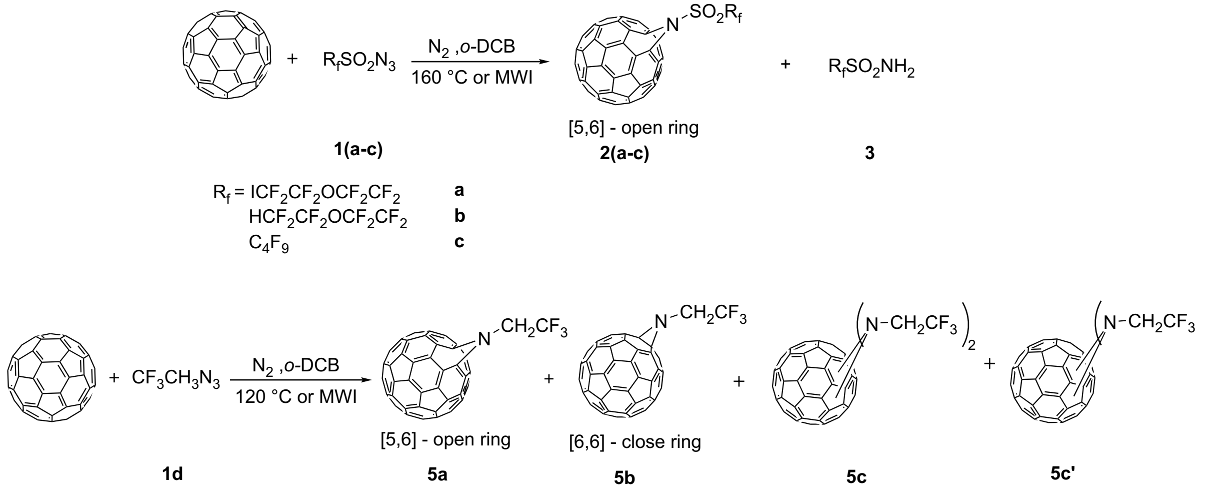


Figure 2. UV–vis spectrum of **2a**, **5a**, and **5b**.

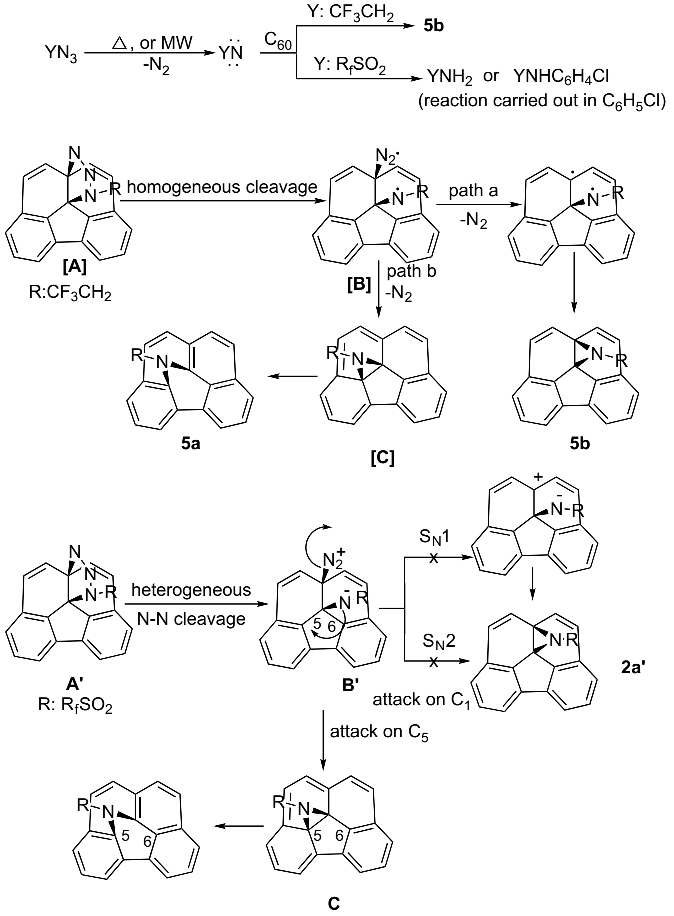
When the reaction was carried out under microwave irradiation, however, only two monoadducts **5a** (38%) and **5b** (19%) were obtained, no multi-addition product was isolated.

All the above reaction results clearly show the difference between the fluorinated sulfonyl azides $R_fSO_2N_3$ **1**(**a**–**c**) with their hydrocarbon analogy RSO_2N_3, while the fluoroalkylazide $CF_3CH_2N_3$ **1d**[20] behaves similar to alkyl or arylazide RN_3. Fluoroalkylazide **1d** added to C_{60} by two pathways. One is the nitrene intermediate added to C_{60} in [1+2] cycloaddition yielding aziridine fullerene **5b**. The another way is the **1d** added to C_{60} by [3+2] cycloaddition to form a triazoline **[A]**, which underwent homogeneous cleavage of the N–N single bond giving a biradical intermediate **[B]**, two possible routes (paths a and b) will lead to **5a** and **5b** as investigated by Luh et al. (see Scheme 1).[21]

In the case of fluoroalkanesulfonyl azides **1**(**a**–**c**) due to the strong electron withdrawing property of R_fSO_2 group, the nitrene intermediate R_fSO_2N did not add to the electron-deficient carbon–carbon double bond of C_{60}, it transformed to the corresponding amine $R_fSO_2NH_2$ or $R_fSO_2NHC_6H_4Cl$ (when the reaction was carried out in C_6H_5Cl) (see Scheme 2). On the other hand the [3+2] cycloaddition product *N*-fluoroalkane-sulfonyl triazoline **[A′]** should undergo N–N bond heterogeneous cleavage to give zwitterion intermediate **[B′]**, which is difficult to release N_2 to form a tertiary carbon cation by an S_N1 process, because both stereo and electron effects are unfavorable, so that it did not give aziridino-fullerene **2a′**. Also the intermediate **[B′]** could not form **2a′** by an S_N2 process, which needed a back attacking on the C_1 by the nitrogen anion RN^-. The only possible pathway is the attacking of the nitrogen anion occurred on the C_5 or C_6 (equivalent in the monoadduct **2**) following the departure of N_2 leading to the adduct **[C]**, which then rearomatized to more stable product azafulleroid **2**.



Scheme 1.



Scheme 2. Possible mechanism for the reaction of **1** with C60 (only relevant section of the fullerene is shown).

3. Conclusion

The reactions of fluoroalkanesulfonyl azides $R_fSO_2N_3$ **1**(**a**–**c**) with [60] fullerene were first investigated. In contrast to their hydrocarbon analogues $CH_3SO_2N_3$ and $C_6H_5CH_2SO_2N_3$, $R_fSO_2N_3$ added to C_{60} to give only [5,6]-azafulleroids with an open cluster structure. While their trifluoroethyl azide $CF_3CH_2N_3$ behaves similar to the alkyl or aryl azides, it reacted with C_{60} affording two monoadducts [5,6]-azafulleroid and [6,6]-aziridino-fullerene, and multiaddition products in good yield. The present reactions afford a convenient method to synthesize a variety of stable fluorinated fullerene derivatives.

4. Experimental

4.1. General remarks

C_{60} was purchased from Wuhan University and in 99% purity. All reactions were performed under nitrogen atmosphere, o-dichlorobenzene, chlorobenzene–carbon disulfide, toluene, and ethyl acetate were used in AR quality. Fluoroalkanesulfonyl azides **1**(**a**–**c**)[22] and trifluoroethyl azide **1d**[20] were prepared according to the literature procedure. ^1H, ^{13}C, and ^{19}F NMR spectra were recorded on Bruker AM-300 or AM-400 instrument with Me_4Si and $CFCl_3$ as the internal standards, respectively. FTIR spectra were obtained with a Nicolet AV-360 spectrophotometer. UV–vis spectra were performed with a UV-2501PC spectrophotometer. ES-MS spectra were performed on a Q-Tof micro-instrument and MALDI-MS spectra were performed on a Voyager-DE STR instrument.

4.2. Reaction of azide 1a with C_{60} in o-DCB

A solution of C_{60} (0.11 g, 0.14 mmol) and **1a** (1.9 g, 1.68 mmol) in 30 mL of o-DCB was heated at 160 °C for 2 h and the solvent was then evaporated under reduced pressure. Chromatography on silica gel (cyclohexane/toluene/dioxane=6:1:0.2) gave unconverted C_{60} (21 mg) and **2a** (38 mg 30%); more polar product $ICF_2CF_2OCF_2CF_2SO_2NH_2$ **3a** (0.9 g) was obtained by using petroleum ether/ethyl acetate (10:1) as eluent. After isolation, product **2a** was further purified by dissolving in CS_2, precipitating with n-pentane, centrifugation, and decanting to remove the pentane soluble components. It was finally dried under vacuum.

4.3. *N*-(5-Iodo-3-oxa-octafluoropentyl)sulfonyl aza[60]fulleroid 2a

FTIR (KBr): 1631, 1410, 1332, 1293, 1138, 1030, 909, 804, 708, 617, 526 cm^{-1}; ^{19}F NMR (471 MHz, $CS_2/CDCl_3$=4:1): δ=−64.78 (t, 2F, $^3J_{F,F}$=6.5 Hz, ICF_2), −80.95 (t, 2F, $^3J_{F,F}$=13.5 Hz, OCF_2), −85.15 to

85.23 (m, 2F, CF_2O), -113.60 (s, 2F, SCF_2); ^{13}C NMR (126 MHz, $CS_2/CDCl_3=4:1$) $\delta=149.08$, 147.23, 145.32, 145.01, 144.58, 144.54, 144.47, 144.45, 144.40, 144.35, 144.27, 144.02, 143.97, 143.83, 143.65, 143.49, 143.16, 143.06, 142.88, 142.01, 141.90, 140.56, 140.07, 139.76, 139.29, 138.89, 137.80, 135.91, 134.70, 134.65, 129.17, 125.90 ($32C_{60}$ sp^2 signals); UV–vis (CH_2Cl_2), λ_{max} (>225 nm, ε): 492 (150), 325 (121,910), 257 (361,390), 227 (283,570); ES-MS: *m*/*z* observed 1140.8 $[M]^-$ (calcd 1140.85).

4.4. *N*-(3-Oxa-1,1,2,2,4,4,5,5-octafluoropentyl)-sulfonyl aza[60]fulleroid 2b

FTIR (KBr): 2921, 2852, 2638, 1540, 1410, 1326, 1283, 1177, 1139, 978, 621, 526 cm^{-1}; ^{1}H NMR (500 MHz, $CS_2/CDCl_3=4:1$): $\delta=5.90$ (t, 1H, $^{2}J_{H,F}=52$ Hz, HCF_2); ^{19}F NMR (471 MHz, $CS_2/CDCl_3=4:1$): $\delta=-80.65$ (t, 2F, $^{3}J_{F,F}=12.2$ Hz, OCF_2), -88.08 to -88.14 (m, 2F, CF_2O), -113.68 (s, 2F, SCF_2), -137.01 (dt, 2F, $^{3}J_{F,F}=4.7$ Hz, $^{2}J_{H,F}=52$ Hz, HCF_2); ^{13}C NMR (126 MHz, $CS_2/CDCl_3=4:1$): $\delta=149.03$, 147.19, 145.27, 144.97, 144.53, 144.49, 144.43, 144.40, 144.35, 144.30, 144.22, 143.98, 143.93, 143.78, 143.60, 143.45, 143.12, 143.02, 142.84, 141.97, 141.85, 140.52, 140.02, 139.71, 139.25, 139.34, 138.85, 138.39, 138.37, 137.75, 135.87, 134.60 ($32C_{60}$ sp^2 signals); UV–vis (CH_2Cl_2), λ_{max} (>220 nm, ε): 529 (230), 325 (114,680), 258 (350,590), 228 (254,950); ES-MS: *m*/*z* observed 1014.9 $[M]^-$ (calcd 1014.95).

4.5. *N*-Perfluorobutanesulfonyl aza[60]fulleroid 2c

FTIR (KBr): 2963, 2921, 1632, 1411, 1345, 1260, 1137, 1100, 1027, 802, 615, 526 cm^{-1}; ^{19}F NMR (471 MHz, $CS_2/CDCl_3=4:1$): $\delta=-80.46$ (t, 3F, $^{3}J_{F,F}=9.0$ Hz, CF_3), -109.90 (m, 2F, CF_2S), -120.43 (m, 2F, CF_2), -125.62 (m, 2F, CF_2); ^{13}C NMR (126 MHz, $CS_2/CDCl_3=4:1$): $\delta=148.96$, 147.13, 145.21, 144.92, 144.47, 144.45, 144.43, 144.36, 144.34, 144.30, 144.23, 144.15, 143.92, 143.87, 143.54, 143.40, 143.13, 143.07, 142.97, 142.78, 141.92, 141.79, 140.46, 139.98, 139.68, 139.15, 138.80, 137.65, 135.81, 130.81, 129.71, 128.86 ($32C_{60}$ sp^2 signals); UV–vis (CH_2Cl_2), λ_{max} (>220 nm, ε): 501 (920), 492 (980), 326 (76,490), 258 (231,500), 228 (164,850), 224 (114,090); ES-MS: *m*/*z* observed 1016.9 $[M]^-$ (calcd 1016.95).

4.6. *N*-1,1,1-Trifluoroethyl aza[60]fulleroid 5a

FTIR (KBr): 2919, 1633, 1506, 1427, 1309, 1265, 1177, 1154, 962, 729, 575, 525 cm^{-1}; ^{1}H NMR (500 MHz, $CS_2/CDCl_3=4:1$): $\delta=4.32$ (q, 2H, $^{3}J_{HF}=8.5$ Hz, CH_2); ^{13}C NMR (126 MHz, $CS_2/CDCl_3=5:1$): $\delta=147.52$, 144.86, 144.70, 144.61, 144.45, 144.32, 144.25, 144.16, 143.89, 143.78, 143.69, 143.57, 143.50, 143.43, 143.25, 143.13, 143.02, 142.93, 142.77, 142.58, 141.45, 140.91, 140.03, 139.51, 138.57, 138.52, 137.98, 137.94, 136.32, 136.24, 135.66, 133.66 ($32C_{60}$ sp^2 signals), 125.06 (CF_3), 54.10 (q, $^{2}J_{CF}=33.2$ Hz, CH_2); ^{19}F NMR (471 MHz, $CS_2/CDCl_3=4:1$): $\delta=-70.63$ (t, $^{3}J_{HF}=8.5$ Hz, CF_3); UV–vis (CH_2Cl_2), λ_{max} (>220 nm, ε): 784 (170), 537 (1960), 405 (7530), 329 (89,360), 258 (303,140), 222 (212,840); MALDI-MS: *m*/*z* observed 817 $[M]^-$ (calcd 817.01).

4.7. *N*-(1,1,1-Trifluoroethyl)aziridino[60]fullerene 5b

FTIR (KBr): 2964, 1713, 1632, 1498, 1387, 1261, 1149, 1096, 1023, 802, 572, 523 cm^{-1}; ^{1}H NMR (500 MHz, $CS_2/CDCl_3=4:1$): $\delta=4.32$ (q, 2H, $^{3}J_{HF}=8.0$ Hz, CH_2); ^{13}C NMR (126 MHz, $CS_2/CDCl_3=5:1$): $\delta=145.16$, 145.09, 144.79, 144.61, 144.44, 144.17, 144.08, 143.81, 143.68, 143.60, 143.49, 142.99, 142.73, 142.01, 141.98, 140.87 ($16C_{60}$ sp^2 signals), 82.31 (C_{60} sp^3 signals), 51.35 (q, $^{2}J_{CF}=32.8$ Hz, CH_2); ^{19}F NMR (471 MHz, $CS_2/CDCl_3=4:1$): $\delta=-69.64$ (t, 3F, $^{3}J_{HF}=8.9$ Hz, CF_3); UV–vis (CH_2Cl_2), λ_{max} (>220 nm, ε): 786 (100), 536 (690), 485 (620), 422 (1220), 404 (2620), 328 (41,640), 257 (153,110), 225 (95,900); MALDI-MS: *m*/*z* observed 817 $[M]^-$ (calcd 817.01).

4.8. Bisiminofullerene 5c

FTIR (KBr): 2922, 2851, 1632, 1555, 1425, 1401, 1310, 1267, 1155, 1054, 1028, 963, 849, 659, 629, 523 cm^{-1}; ^{1}H NMR (500 MHz, $CS_2/CDCl_3=4:1$): $\delta=4.26$ (q, 4H, $^{3}J_{HF}=8.3$ Hz, CH_2); ^{13}C NMR (126 MHz, $CS_2/CDCl_3=5:1$): $\delta=147.32$, 146.47, 145.20, 145.06, 144.96, 144.81, 144.77, 144.51, 144.03, 143.38, 142.80, 142.77, 142.68, 143.66, 142.10, 141.49, 140.90, 140.67, 140.33, 140.07, 139.16, 138.65, 137.07, 136.66, 135.60,131.90,131.10,130.78 ($28C_{60}$ sp^2 signals), 81.69 (C_{60} sp^3 signals), 64.69 (CH_2); ^{19}F NMR (471 MHz, $CS_2/CDCl_3=4:1$): $\delta=-70.07$ (t, $^{3}J_{HF}=8.0$ Hz, CF_3); UV–vis (CH_2Cl_2), λ_{max} (>220 nm, ε): 772 (43), 536 (375), 330 (7315), 262 (21,666), 228 (20,253); MALDI-MS: *m*/*z* observed 915.3 $[M+H]^-$ (calcd 914.03).

4.9. Trisiminofullerene 5c′

FTIR (KBr): 2963, 2923, 2853, 1723, 1634, 1461, 1380, 1262, 1097, 1022, 801, 701, 516 cm^{-1}; ^{1}H NMR (500 MHz, $CS_2/CDCl_3=4:1$): $\delta=4.26$ (q, 4H, $^{3}J_{HF}=8.3$ Hz, CH_2), 4.36 (q, 2H, $^{3}J_{HF}=8.5$ Hz, CH_2); ^{13}C NMR(126 MHz, $CS_2/C_6D_6=1:2$): $\delta=148.58$, 148.31, 146.66, 146.08, 145.58, 145.52, 145.16, 145.05, 144.93, 144.87, 144.61, 144.58, 144.53, 144.42, 144.28, 144.11, 143.42, 142.77, 142.45, 142.41, 141.98, 141.23, 140.54, 139.04, 137.86, 136.39,135.72, 135.46, 133.86 ($30C_{60}$ sp^2 signals), 82.83 (C_{60} sp^3 signals), 65.99 (CH_2); ^{19}F NMR (471 MHz, $CS_2/CDCl_3=4:1$): $\delta=-69.60$ (t, $^{3}J_{HF}=9.4$ Hz, CF_3), -70.58 (t, $^{3}J_{HF}=8$ Hz, CF_3); UV–vis (CH_2Cl_2), λ_{max} (>220 nm, ε): 536 (437), 484 (498), 322 (11,643), 257 (34,952), 227(34,071). ES-MS: *m*/*z* observed 1012 $[M+H]^-$ (calcd 1011.05).

4.10. Reaction of 1a with C_{60} under microwave irradiation condition

A solution of C_{60} (0.11 g, 0.14 mmol), **1a** (1.76 g, 1.54 mmol), and *o*-DCB (20 mL in a 50 mL three necked flask) was irradiated under microwave (700 W) for 20 min under N_2 atmosphere. As the thermal reaction similar work-up gave **2a** (41 mg 32%) and **3a** (0.9 g), and 18 mg of unreacted C_{60} was recovered.

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References and notes

1. Prato, M.; Li, Q. C.; Wudl, F.; Lucchini, V. *J. Am. Chem. Soc.* **1993**, *115*, 1148–1150.
2. Takeshita, M.; Suzuki, T.; Shinkai, S. *J. Chem. Soc., Chem. Commun.* **1994**, 2587–2588.
3. Hummeien, J. C.; Prato, M.; Wudl, F. *J. Am. Chem. Soc.* **1995**, *117*, 7003–7004.
4. Yan, M.; Cai, S. X.; Keana, J. F. W. *J. Org. Chem.* **1994**, *59*, 5951–5954.
5. Averdung, J.; Wolff, C.; Mattay, J. *Tetrahedron Lett.* **1996**, *37*, 4683–4684.
6. Shen, C. K. F.; Chien, K. M.; Juo, C. G.; Her, G. R.; Luh, T. Y. *J. Org. Chem.* **1996**, *61*, 9242–9244.
7. Averdung, J.; Mattay, J. *Tetrahedron* **1996**, *52*, 5407–5420.
8. Averdung, J.; Jorres-Garica, G.; Laftmann, H.; Schlachter, J.; Mattay, J. *Fullerene Sci. Technol.* **1996**, *4*, 633–654.
9. Averdung, J.; Mattay, J.; Jacovi, D.; Abraham, W. *Tetrahedron* **1995**, *51*, 2543–2552.
10. Ulmer, L.; Mattay, J. *Eur. J. Org. Chem.* **2003**, 2933–2940.
11. He, P.; Zhu, S. Z. *J. Fluorine Chem.* **2004**, *125*, 1529–1536.
12. He, P.; Zhu, S. Z. *Mini-Rev. Org. Chem.* **2004**, *1*, 417–435.
13. Zhu, S. Z.; He, P. *Tetrahedron* **2005**, *61*, 5679–5685.
14. He, P.; Zhu, S. Z. *J. Fluorine Chem.* **2005**, *126*, 825–830.
15. He, P.; Zhu, S. Z. *Tetrahedron* **2006**, *62*, 549–555.
16. Reed, C. A.; Bolskar, R. D. *Chem. Rev.* **2000**, *100*, 1075–1120.
17. Pato, M.; Wudl, Q. F.; Lucchini, V.; Maggini, M.; Stimpfe, E.; Scorrane, G.; Suznki, J. *J. Am. Chem. Soc.* **1993**, *115*, 8479–8480.
18. Suzuki, T.; Li, Q.; Khemani, K. C.; Wudl, F. *J. Am. Chem. Soc.* **1992**, *114*, 7301–7302.
19. Isaacs, L.; Wehrsig, A.; Diederich, F. *Helv. Chim. Acta* **1993**, *76*, 1231–1250.
20. Wu, Y. M.; Deng, J.; Li, Y.; Chen, Q. Y. *Synthesis* **2005**, *8*, 1314–1318.
21. Shen, C. K. F.; Yu, H. H.; Juo, C. G.; Chien, K. M.; Her, G. R.; Luh, T. Y. *Chem.—Eur J.* **1997**, *3*, 744–748.
22. Zhu, S. Z. *J. Chem. Soc., Perkin Trans. 1* **1994**, 2077–2081.